REACTIVITY OF URACIL IN THE GAS PHASE: STATISTICAL & NON-STATISTICAL STUDY

Estefania Rossich Molina, Emilio Martinez-Nuñez, Jean-Yves Salpin, Riccardo Spezia

REACTIVITY OF URACIL IN THE GAS PHASE: STATISTICAL & NON-STATISTICAL STUDY

Estefania **ROSSICH MOLINA** [a,b], E. **MARTINEZ-NUÑEZ** [c], Jean-Yves **SALPIN** [a,b] and R. **SPEZIA** [a,b]

a- LAMBE, CEA, CNRS, Université Paris Saclay, F-91025, Evry, France
b- LAMBE, Université d'Evry, F-91025, Evry, France
c- University of Santiago de Compostela, Physical Chemistry, Santiago de Compostela, Spain

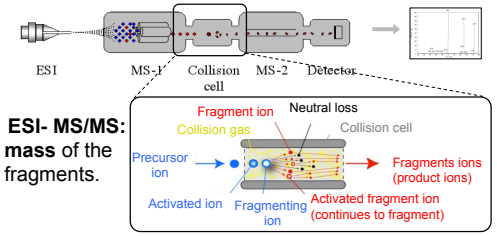
OVERVIEW

- The study of the reactivity of biomolecules in the gas phase allows to get rid of the efects of the environment: **intrinsic properties** of molecules.
- Using Collision Induced Dissociation experiments and Chemical Dynamics simulations we obtained reaction mechanisms for protonated Uracil.

INTRODUCTION

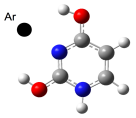
- Explain non-statistical and statistical reactivity of protonated Uracil in the gas phase and obtain predictive MS-MS spectra.

METHODS



ESI- MS/MS: mass of the fragments.

QM-MM CHEMICAL DYNAMICS SIMULATIONS [1]: non-statistical mechanisms



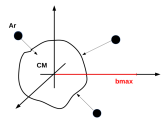
Collision system

Potential energy function

$V = V_{ion} + V_{Ar\text{-}ion}$

QM: AM1, PM3 and DFT

MM



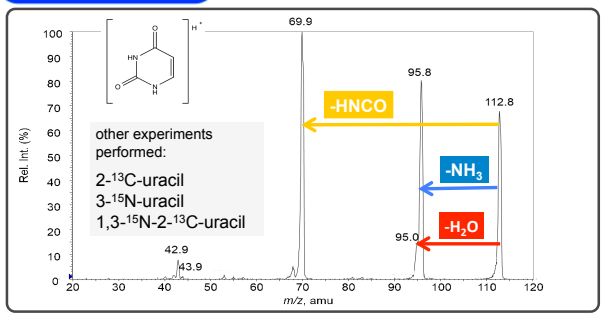
Ensemble of trajectories

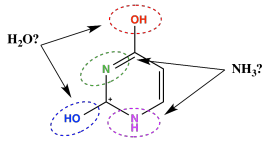
RRKM and KINETIC MONTE CARLO (KMC) SIMULATIONS: statistical reactivity.

- For trajectories that did not react before IVR (intramolecular vibrational relaxation) takes place but have enough energy to react later on.
- Following automatic protocol[3] to find all fragmentation pathways, **TSs** and **minima**. Then this is used as input for RRKM and KMC simulations.

RESULTS

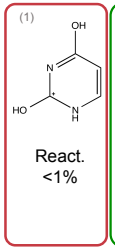
Experiments



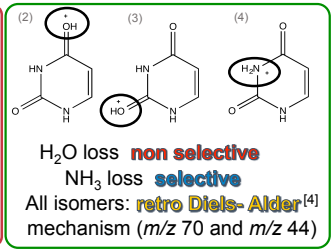


from RRKM analysis:
H⁺ transfer
ns
(out of simulation time)

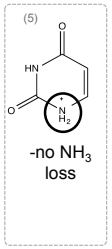
Chemical Dynamics Simulations[2]



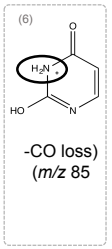
React. <1%



H_2O loss **non selective**
NH_3 loss **selective**
All isomers: **retro Diels- Alder** [4] mechanism (*m/z* 70 and *m/z* 44)

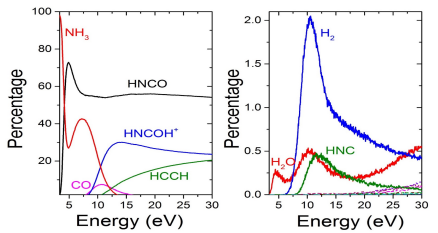


-no NH_3 loss

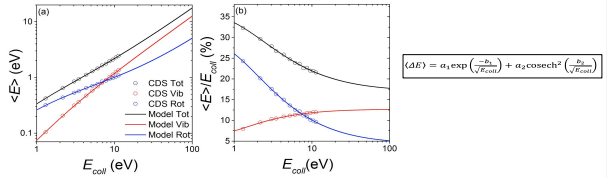


-CO loss) (*m/z* 85

RRKM and KMC



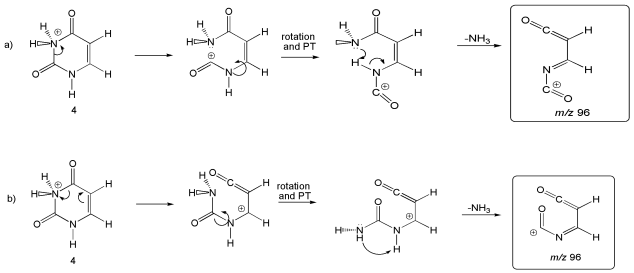
Product yields of the different fragmentation channels of the $C_4H_5N_2O_2^+$ system obtained in the KMC simulation as a function of the excitation energy.



$\langle \Delta E \rangle = a_1 \exp\left(\frac{-b_1}{\sqrt{E_{coll}}}\right) + a_2 \mathrm{cosech}^2\left(\frac{b_2}{\sqrt{E_{coll}}}\right)$

a) Average final (internal) energies of $[uracil]H^+$ as a function of the collision energy (in the center of mass framework) for Ar + $[uracil]H^+$ collisional system.
b) (b) Percent energy transfer values to $[uracil]H^+$ internal degrees of freedom. Symbols and solid lines correspond to the chemical dynamics simulation (CDS), and energy transfer model results, respectively. [5]

Example of NH_3 loss mechanism for isomer 4.



CONCLUSIONS

- As suggested by experiments, *m/z* 70 is obtained by a retro Diels-Alder (rDA) mechanism.
- rDA reaction does not follow the minimum energy path along the reaction coordinate, while stepwise mechanisms do. In experiments, both mechanisms can co-exist.
- Initial protonation state of the ion plays a crucial role in determining the fragmentation pathway.
- NH_3 loss is a selective reaction, while H_2O loss it is not.

Refs.:
[1] Hase et al. JPCA (1999)
[2] Rossich Molina et al. J. Mass Spectrom. (2015)
[3] Martinez Nuñez. Phys. Chem. Chem. Phys. (2015)
[4] Diels and Alder. Chemische Berichte. (1929)
[5] Rossich Molina et al. PCCP (2016)

ASMS, San Antonio, Texas 2016